



## Research paper

# Effect of the calcination temperature on the visible light photocatalytic activity of direct contact Z-scheme $\text{g-C}_3\text{N}_4\text{-TiO}_2$ heterojunction

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## ABSTRACT

Z-scheme  $\text{g-C}_3\text{N}_4\text{-TiO}_2$  heterojunctions containing  $\text{g-C}_3\text{N}_4$  nanosheets with different thickness were prepared by sintering the mixture of  $\text{g-C}_3\text{N}_4$  and nanotube titanic acid (denoted as NTA) at different temperatures in air. As-prepared Z-scheme  $\text{g-C}_3\text{N}_4\text{-TiO}_2$  heterojunctions were characterized by X-ray diffraction, transmission electron microscopy, atomic force microscopy, X-ray photoelectron spectroscopy, ultraviolet-visible light diffuse reflectance spectrometry, electron spin resonance, and photoluminescence spectrometry. Findings indicate that the annealing temperature has crucial effects on the visible-light photocatalytic activity ( $\lambda \geq 420 \text{ nm}$ ) of the as-prepared Z-scheme  $\text{g-C}_3\text{N}_4\text{-TiO}_2$  heterojunctions. The  $\text{Ti}^{3+}$  and porous  $\text{g-C}_3\text{N}_4$  nanosheets formed upon the calcination at  $600^\circ\text{C}$  as well as the low concentration of bulk single-electron trapped oxygen vacancy are favorable to the transport of the photoexcited charge carriers. This, in association with the Z-scheme system, contributes to improving the photocatalytic activity of  $\text{g-C}_3\text{N}_4\text{-TiO}_2$  photocatalysts. As a result,  $\text{g-C}_3\text{N}_4\text{-TiO}_2$  photocatalyst prepared at  $600^\circ\text{C}$  exhibits good photocatalytic activity towards the degradation of propylene and hydrogen generation by water-splitting under visible light irradiation.

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## 1. Introduction

As the well known photocatalyst, anatase  $\text{TiO}_2$  has been investigated extensively due to its good stability, low cost and strong oxidation ability [1]. However, anatase  $\text{TiO}_2$  with a wide band-gap needs to be excited by ultraviolet, while its high photoinduced electron-hole recombination rate is harmful to photocatalytic activity. The two defects seriously confined its practical application in environmental governance [2]. To improve its visible light absorption and activity, metal doping [3,4], non-metal doping [5–7], metal and nonmetal codoping [8,9] as well as  $\text{Ti}^{3+}$  and oxygen vacancy self-doped [10–12] were all the effective methods. Unfortunately, metal doping especially noble metal doping is often less cost-effective, while non-metal doping is usually less efficient in increasing the photocatalytic activity of  $\text{TiO}_2$ . Moreover, although the method of metal and nonmetal codoping can

effectively improve activity, but there still exists the problem of preparation process complex and high cost. So coupling  $\text{TiO}_2$  with other narrow band-gap semiconductors is found to be an efficient way [13–15].

In recent years, graphite-phase carbon nitride ( $\text{g-C}_3\text{N}_4$ ) has acquired highly concern of many researchers in the world on account of the unique two-dimensional planar structure, high physicochemical stability, easy synthesis, low cost and the relatively narrow band-gap (2.7 eV), and has been widely used for hydrogen generation by water-splitting [16],  $\text{CO}_2$  reduction [17] or organic pollutant degradation [18] under visible light irradiation. Nevertheless, single bulk  $\text{g-C}_3\text{N}_4$  currently has very low activity due to its high photogenerated electrons-holes recombination efficiency and small specific surface area [19,20]. To deal with these issues, some researchers tried to combine bulk  $\text{g-C}_3\text{N}_4$  with semiconductor materials, thereby obtaining thin  $\text{g-C}_3\text{N}_4$  nanosheets with improved visible light utilization efficiency [21–24]. Especially, due to its non-toxic, stabilization, metal-free and excellent visible absorption ability,  $\text{g-C}_3\text{N}_4$  could be used as a good photosensitizer to enhance the visible light activity of the wide band-gap semiconductor such as  $\text{TiO}_2$  [13–15,25–29]. However, most of

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these studies mainly focused on the building of heterojunction (traditional [21,22] or Z scheme [17,18,23]) between the appropriate energy band materials and there was little research to study the influence of the g-C<sub>3</sub>N<sub>4</sub> structure itself in the composites to the photocatalysis. In fact, the thickness and porosity of g-C<sub>3</sub>N<sub>4</sub> nanosheets had important impact to the light absorption, charge carriers transport efficiency and specific surface area and then would further affect the photocatalysis activity. Niu et al. [30] prepared the remarkably improved photocatalytic activities of g-C<sub>3</sub>N<sub>4</sub> nanosheets with a thickness of around 2 nm by thermal oxidation etching of bulk g-C<sub>3</sub>N<sub>4</sub> in air. Yang et al. [31] and Lin et al. [32] separately employed liquid phase solvents exfoliation bulk g-C<sub>3</sub>N<sub>4</sub> to prepare the few-layered or monolayer g-C<sub>3</sub>N<sub>4</sub> nanosheets which both displayed the enhanced visible light photocatalytic activities.

In this article, we select g-C<sub>3</sub>N<sub>4</sub> to modify the novel-TiO<sub>2</sub> (obtained by the dehydration of nanotube titanic acid (denoted as NTA)) possessing a certain degree of visible light absorption and a large amount of single-electron-trapped oxygen vacancy, hoping to construct Z-scheme g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub> heterojunction photocatalysts by simple solid sintering method. Due to the fact that the photocatalytic activity of the obtained composites with different heating temperatures had the considerable difference, we discussed the effect of the annealing temperature to the band structure, the thickness of g-C<sub>3</sub>N<sub>4</sub> nanosheets, optical absorption and charge carriers transport performance of the nanocomposites in detail by systematic characterization and proposed the possible mechanism.

## 2. Experimental

### 2.1. Materials and methods

All the raw materials were analytical reagent and did not make any further treatment. The details about the preparation of NTA, bulk g-C<sub>3</sub>N<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub> nanosheets and g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub> composites are available in our previous published work [33]. Namely, NTA was prepared by TiO<sub>2</sub> (P25) in the concentrated alkaline hydrothermal treatment for 24 h at 150 °C while the samples of bulk g-C<sub>3</sub>N<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub> nanosheets and x%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-y composites (x denoted the mass percentage of g-C<sub>3</sub>N<sub>4</sub> in the mixture of bulk g-C<sub>3</sub>N<sub>4</sub> and NTA and y represented the calcination temperature) were obtained by simple high temperature calcination in air. Specifically, bulk g-C<sub>3</sub>N<sub>4</sub> was prepared by calcining melamine at 550 °C for 2 h, and g-C<sub>3</sub>N<sub>4</sub> nanosheets was acquired by heating the bulk g-C<sub>3</sub>N<sub>4</sub> at 600 °C for 2 h in air.

### 2.2. Characterization

The crystal structure of the photocatalysts were confirmed by X-ray diffractometer (XRD, Bruker D8-ADVANCE, Germany; Cu-K<sub>α</sub> radiation ( $\lambda = 0.15418 \text{ nm}$ ), 40 kV and 40 mA). The morphology of the samples was obtained by transmission electron microscopy (TEM, JEOL JEM-2100, Japan) and an atomic force microscope (AFM, Bruker Dimension Icon, Germany). The BET (Brunauer, Emmett and Teller) specific surface area was determined by nitrogen adsorption-desorption isotherms (Quadasorb SI instrument, USA). The thermal stability of g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub> photocatalysts in the temperature range of 25–1000 °C was evaluated by thermogravimetric analysis (TGA; SDTA 851e, Switzerland) at a heating rate of 10 °C min<sup>-1</sup> in air. X-ray photoelectron spectroscopy (XPS) test was carried out on a Thermo ESCALAB 250Xi spectrometer (USA; the binding energy of contaminant carbon (284.8 eV) was used as the reference). The UV-vis diffuse reflection spectra were recorded on a Shimadzu UV-2600 UV/Vis spectrophotometer (Japan; BaSO<sub>4</sub> as reference sample). Electron spin resonance (ESR) spectra were tested on a spectrometer (Bruker EMX-10/12,

Germany) with a 100 kHz field modulation, a 1.0 G amplitude modulation and a 20.4 mW microwave power at room temperature in air. The fluorescence emission spectra were measured on the F-7000 FL spectrophotometer with the excitation wavelength of 315 nm. The time-resolved fluorescence decay spectra were studied by an FLS980 fluorescence spectrophotometer (295 nm laser excitation, England).

### 2.3. Photocatalytic activity tests and photoelectrochemical measurements

The photocatalytic activity was evaluated by monitoring the oxidation of propylene oxidation under visible light irradiation [33,34]. The light source was a 300 W xenon lamp (PLS-SXE300/300UV) with a 420 nm cutoff filter ( $\lambda \geq 420 \text{ nm}$ ). The degradation rate of propylene was calculated according to the change of concentration for C<sub>3</sub>H<sub>6</sub> before and after visible light illumination which was detected by a gas chromatograph (Shimadzu GC-9A, Japan) equipped with a flame ionization detector.

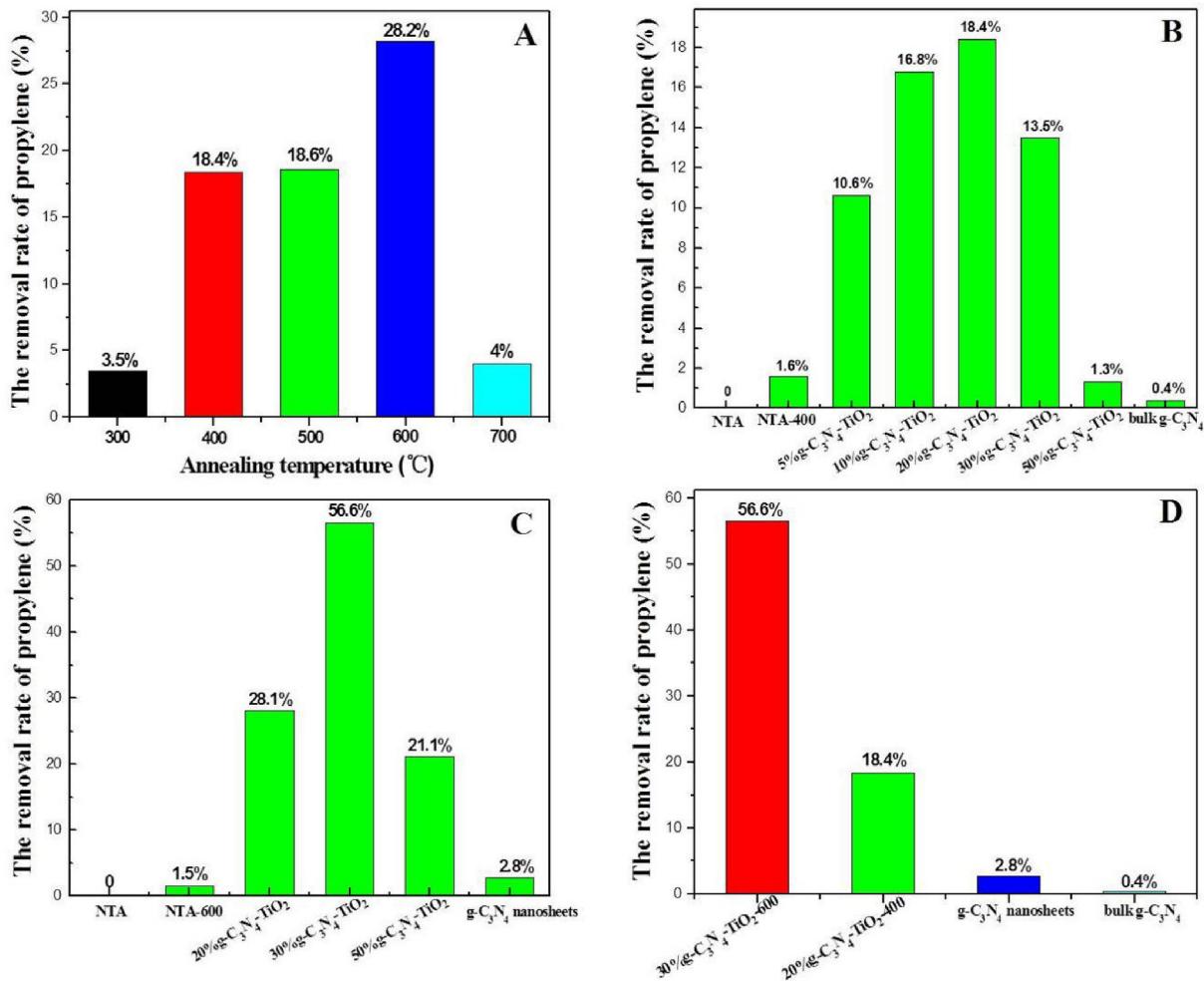
The photocurrent-time curve was measured by an electrochemical workstation (CHI600E China; a standard three-electrode photoelectrochemical cell with 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution as the electrolyte was adopted) under the periodic illumination at a definite time interval. About 20 mg sample was first put into 0.5 mL of ethanol and ultrasonic dispersed for 20 min. Then the paste was coated onto the conducting glass and dried at 120 °C for 3 h in the oven. Lastly, the conducting glass with coated samples and platinum wire were used as working and counter electrodes respectively and a saturated calomel electrode (SCE) was used as the reference electrode. Before measurement the electrolyte was purged by inletting argon for 20 min to get rid of the dissolved oxygen. The light source was the same as the photocatalytic activity measurement.

## 3. Results and discussion

### 3.1. The photocatalytic activity

To investigate the influence of the annealing temperature to the composites photocatalytic activity, we prepared a series of 20%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub> composites under different temperatures. As seen from Fig. 1A, the photocatalytic activity of 20%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub> composites tend to rise initially and decrease later with elevating calcination temperatures. Especially, 20%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-400 and 20%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-500 exhibit similar low photocatalytic activity, while 20%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-600 exhibits the best photocatalytic activity. The reason could be that g-C<sub>3</sub>N<sub>4</sub> was very stable below 600 °C, but it would partially decompose to form thin g-C<sub>3</sub>N<sub>4</sub> nanosheets in air at 600 °C [33]. Moreover, NTA would dehydrate to form novel anatase TiO<sub>2</sub> which contained large amounts of single-electron-trapped oxygen vacancy (denoted as V<sub>o</sub><sup>•</sup>) when the temperature exceeded 300 °C [35]. So the sample of 300 °C had the poor crystallinity (seen in Fig. 2B) for the incomplete dehydration which resulted in the very low photoactivity. According to Fig. S3 in the supporting information, g-C<sub>3</sub>N<sub>4</sub> would almost decompose completely at 700 °C and Fig. 2B indicated that rutile TiO<sub>2</sub> appeared in the sample of 20%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-700 which usually had very poor photoactivity.

So we respectively selected 400 °C (g-C<sub>3</sub>N<sub>4</sub> stable exists) and 600 °C (g-C<sub>3</sub>N<sub>4</sub> partially decomposes) as the annealing temperature to study the effect of g-C<sub>3</sub>N<sub>4</sub> concentration to the photoactivity (seen in Fig. 1B and C). According to the results of Fig. 1B and C, the composites photoactivity both showed rising first and falling later with the increase of g-C<sub>3</sub>N<sub>4</sub> content and 20%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-400 and



**Fig. 1.** Photocatalytic activity of various as-prepared photocatalysts for the photo-oxidation of propylene under visible light ( $\lambda \geq 420$  nm) illumination: (A) 20% g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub> obtained at different annealing temperatures, (B) g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-400 composites with different content of g-C<sub>3</sub>N<sub>4</sub>, (C) g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-600 composites with different content of g-C<sub>3</sub>N<sub>4</sub>, (D) 20%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-400 and 30%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-600 composites as well as bulk g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub> nanosheets.

30%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-600 were the optimum activity samples at 400 °C or 600 °C respectively.

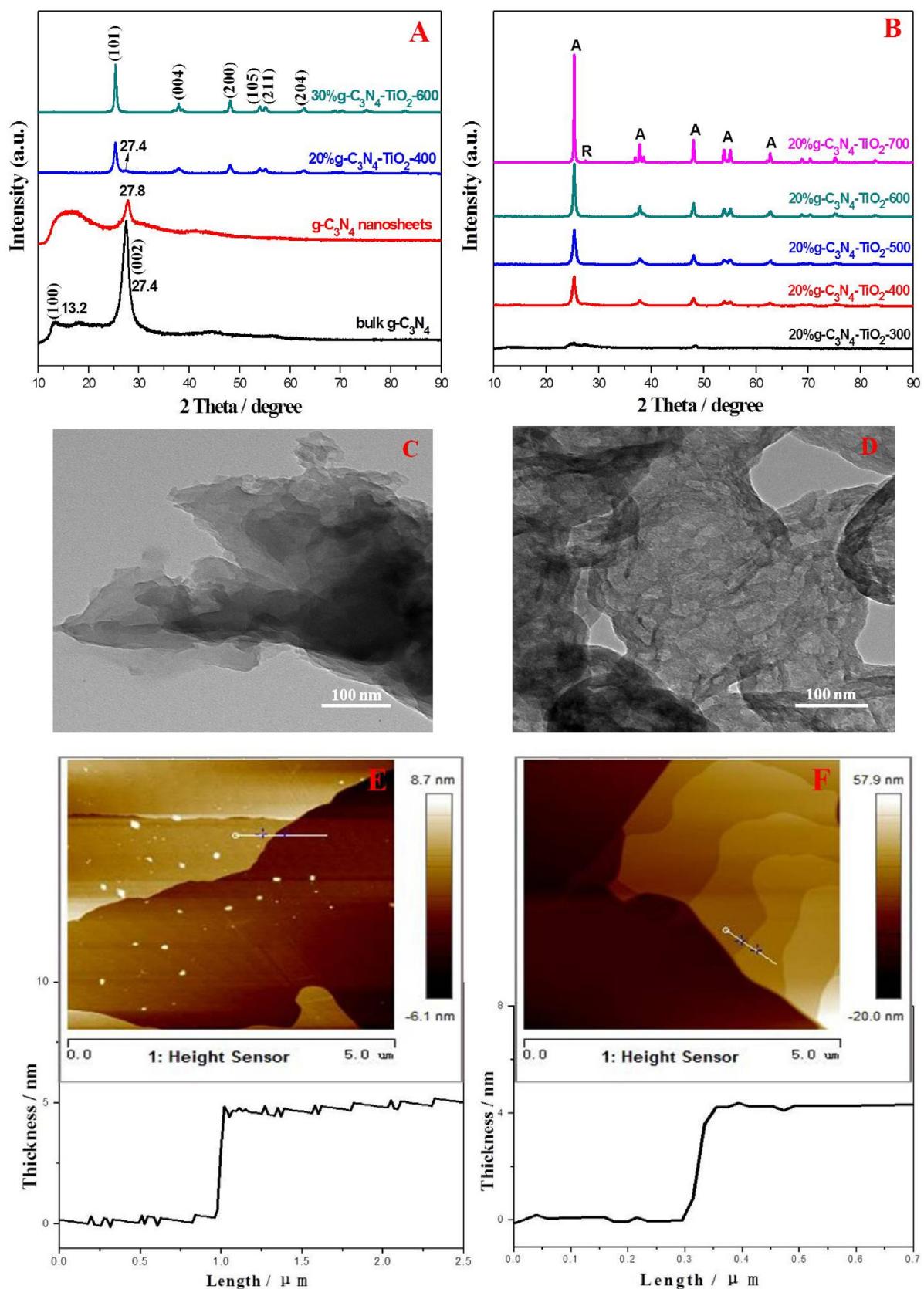
Fig. 1D demonstrated that the activity of 30%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-600 and 20%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-400 for propylene oxidation were about 20 times and 6.6 times higher respectively than that of g-C<sub>3</sub>N<sub>4</sub> nanosheets and the bulk g-C<sub>3</sub>N<sub>4</sub> had the worst activity for the high electrons-holes recombination rate and the very small specific surface area (ca. 10m<sup>2</sup>/g, seen in Table S1). In addition, the results of hydrogen generation by water-splitting also showed that the activity of 30%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-600 was twice than that of 20%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-400 with loading 1%Pt under UV-vis light or visible light illumination (seen in Fig. S1).

On the basis of above analysis, we selected the samples with the optimum photocatalytic activity at 400 and 600 °C respectively to investigate the reason for the vast difference of activity. The specific reason would be expounded in detail in the subsequent section.

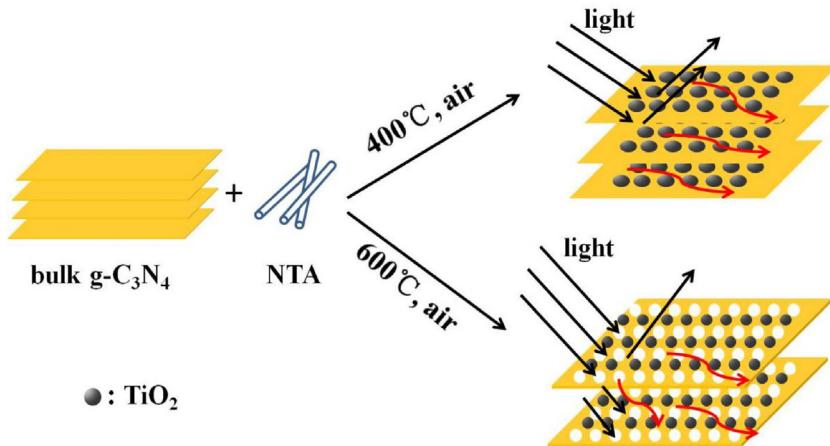
### 3.2. Effect of the calcination temperature on the morphology and structure of the g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub> composites

In order to make certain the large photoactivity difference between the two samples of 400 and 600 °C, we performed the tests of XRD, TEM and AFM. The low magnification and high resolution TEM images of 20%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-400 and 30%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-600 (seen in Fig. S2) indicated that TiO<sub>2</sub> nanoparticles exhibit irregular

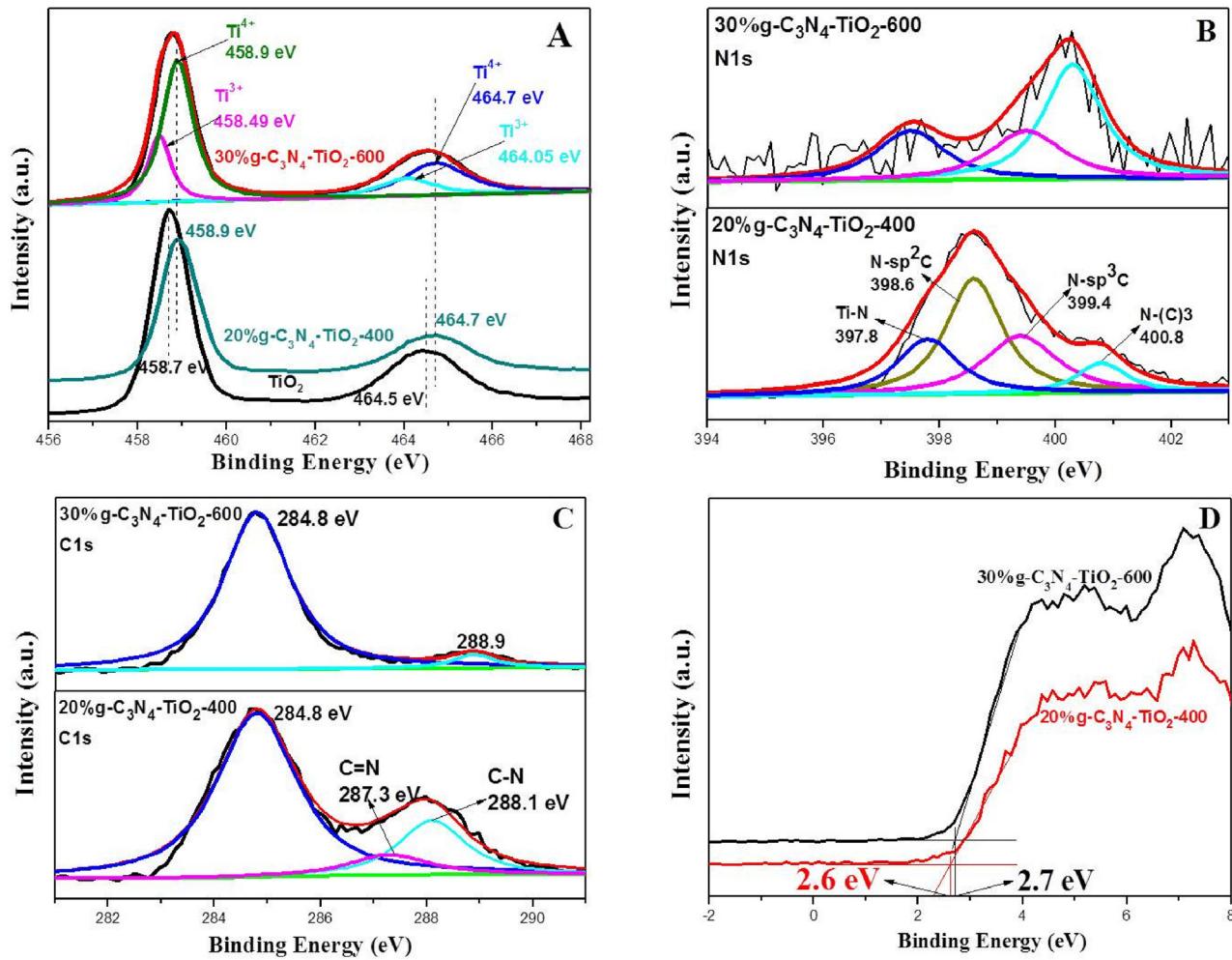
morphology while g-C<sub>3</sub>N<sub>4</sub> present sheet-like appearance. Besides, the two kinds of photocatalysts show clear lattice fringes of TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>, which demonstrates that TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> are well integrated in the g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub> composites. The crystal structure of the composites was determined by the method of X-ray diffraction as shown in Fig. 2A and B. It could be seen that there were two characteristic peaks corresponding to (100) and (002) lattice plane respectively in the bulk g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub> nanosheets. However, it only showed the specific peaks of the anatase TiO<sub>2</sub> but the peaks of g-C<sub>3</sub>N<sub>4</sub> were not observed or inconspicuous in the samples of 30%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-600 and 20%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-400. That should be due to the very low content of g-C<sub>3</sub>N<sub>4</sub> in the composites (seen the TG results in Fig. S3). In order to discern the morphology of g-C<sub>3</sub>N<sub>4</sub> in the composites of 400 and 600 °C, we calcined the samples of g-C<sub>3</sub>N<sub>4</sub>-400 and g-C<sub>3</sub>N<sub>4</sub>-600 by heating bulk g-C<sub>3</sub>N<sub>4</sub> at 400 and 600 °C respectively. The effect of the calcination temperature on the morphology of g-C<sub>3</sub>N<sub>4</sub> was shown in Fig. 2C and D. The bulk g-C<sub>3</sub>N<sub>4</sub>-400 showed the plane layered structure while g-C<sub>3</sub>N<sub>4</sub>-600 presented polyporous construction with curly edge arising from the minimality of the surface energy for g-C<sub>3</sub>N<sub>4</sub> nanosheets. This indicated that the thickness of bulk g-C<sub>3</sub>N<sub>4</sub>-400 was thicker than that of g-C<sub>3</sub>N<sub>4</sub>-600. In addition, the AFM images in Fig. 2E and F demonstrated that the thickness of g-C<sub>3</sub>N<sub>4</sub> nanosheets was about 5 nm and 4 nm in the samples of 400 and 600 °C respectively and diminished with the increase of annealing temperature. The imporous plane struc-



**Fig. 2.** XRD patterns of (A) the as-prepared photocatalysts and (B) samples in the 20% of  $\text{g-C}_3\text{N}_4\text{-TiO}_2$  with different annealing temperature, TEM images of (C)  $\text{g-C}_3\text{N}_4\text{-400}$  and (D)  $\text{g-C}_3\text{N}_4\text{-600}$  and the AFM images of (E) 20%  $\text{g-C}_3\text{N}_4\text{-TiO}_2\text{-400}$  and (F) 30%  $\text{g-C}_3\text{N}_4\text{-TiO}_2\text{-600}$ .



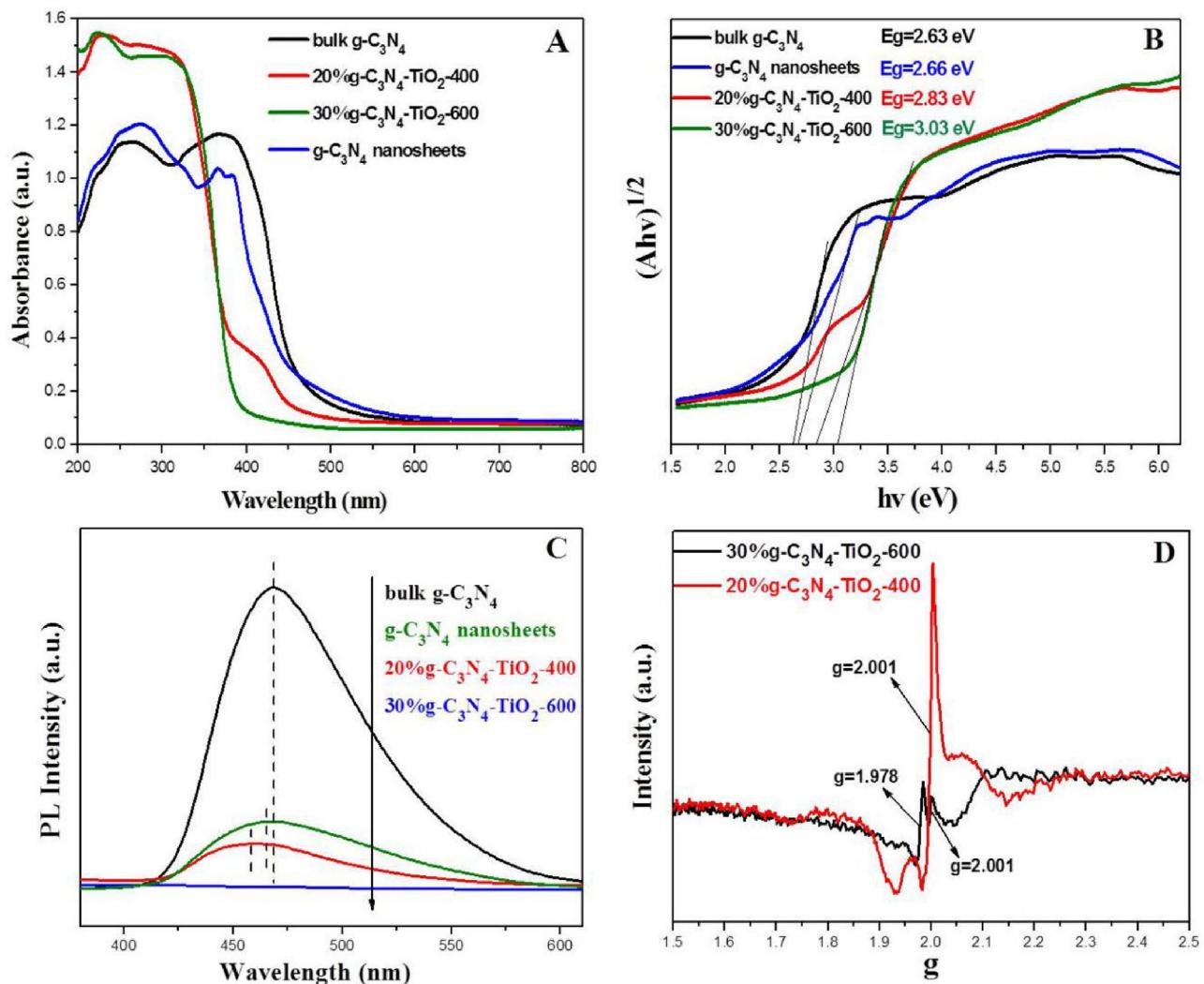
**Fig. 3.** The schematic diagram of the photocatalytic mechanism in  $\text{g-C}_3\text{N}_4\text{-TiO}_2$  photocatalysts obtained by different calcination temperature treatment was proposed under visible light illumination.



**Fig. 4.** High-resolution XPS spectra of (A) Ti2p, (B) N1s, (C) C1s, and (D) valence band spectra of  $\text{g-C}_3\text{N}_4\text{-TiO}_2$  samples.

ture made the transfer of photoinduced carrier only along in-plane direction while the thinner and porous  $\text{g-C}_3\text{N}_4$  nanosheets usually provided plentiful exposed surfaces, numerous active sites, a short transport length for increasing the separation efficiency of interface photoexcited carrier [30–32] and the more irradiation of the incident light. This might explain why 30% $\text{g-C}_3\text{N}_4\text{-TiO}_2$ -600 sample had the much higher activity than 20% $\text{g-C}_3\text{N}_4\text{-TiO}_2$ -400 (schematic diagram seen in Fig. 3).

XPS spectra were utilized to analysis the elemental composition and discern the chemical state of elements in  $\text{g-C}_3\text{N}_4\text{-TiO}_2$  nanocomposites. From the results of Fig. S5, it could be inferred that there were only four elements in the composites although the intensity of N element in the sample of 30% $\text{g-C}_3\text{N}_4\text{-TiO}_2$ -600 was very weak. It should be attributed to the very little retained N atoms in the thermal oxidation treatment process [30,33]. Fig. 4A was the comparison data of the XPS Ti 2p spectra of  $\text{TiO}_2$ ,



**Fig. 5.** (A) UV-vis diffuse reflectance spectra, (B) The plots of transformed Kubelka-Munk functions versus the light energy, (C) The fluorescence emission spectra of the as-prepared samples and (D) ESR spectra of 30% $\text{g-C}_3\text{N}_4$ -TiO<sub>2</sub>-600 and 20% $\text{g-C}_3\text{N}_4$ -TiO<sub>2</sub>-400 samples measured at room temperature in air.

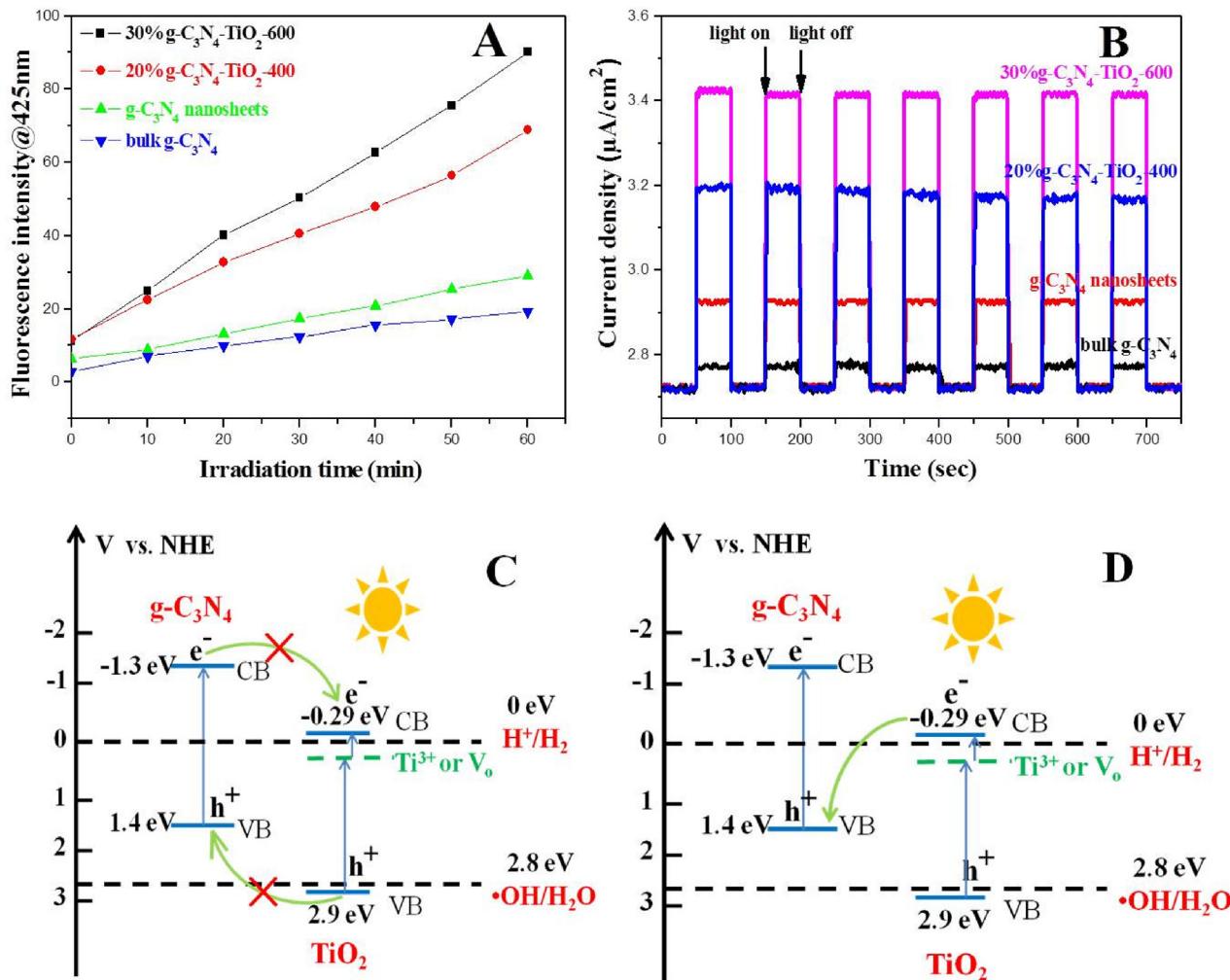
20% $\text{g-C}_3\text{N}_4$ -TiO<sub>2</sub>-400 and 30% $\text{g-C}_3\text{N}_4$ -TiO<sub>2</sub>-600. The Ti 2p peak of 30% $\text{g-C}_3\text{N}_4$ -TiO<sub>2</sub>-600 can be divided into four peaks; and in particular, the peaks at 458.49 eV and 464.05 eV can be assigned to Ti<sup>3+</sup> 2p<sub>3/2</sub> and Ti<sup>3+</sup> 2p<sub>1/2</sub>, which gives evidences to the existence of Ti<sup>3+</sup> in 30% $\text{g-C}_3\text{N}_4$ -TiO<sub>2</sub>-600. Moreover, as compared with that of commercial TiO<sub>2</sub>, the Ti 2p peaks of 20% $\text{g-C}_3\text{N}_4$ -TiO<sub>2</sub>-400 and 30% $\text{g-C}_3\text{N}_4$ -TiO<sub>2</sub>-600 tend to shift towards higher binding energy by about 0.2 eV, possibly due to the interaction between TiO<sub>2</sub> and  $\text{g-C}_3\text{N}_4$  [27].

According to the comparison of N1s spectra of the samples obtained at 400 °C and 600 °C (seen in Fig. 4B), there were four N1s signal peaks located at about 397.8, 398.6, 399.4 and 400.8 eV corresponding to Ti-N bond, pyridine-like (N-sp<sup>2</sup>C) nitrogen, pyrrole-like (N-sp<sup>3</sup>C) nitrogen and graphitic nitrogen respectively [36,37] in the sample of 20% $\text{g-C}_3\text{N}_4$ -TiO<sub>2</sub>-400. While the peak of pyridine-like (N-sp<sup>2</sup>C) nitrogen located at 398.6 eV disappeared and the intensity of graphitic nitrogen peak obviously increased in 30% $\text{g-C}_3\text{N}_4$ -TiO<sub>2</sub>-600 sample. That indicated that pyridine-like nitrogen would transform into graphitic nitrogen when the annealing temperature exceeded the decomposition temperature of  $\text{g-C}_3\text{N}_4$ . Fig. 4B also illustrated that pyridine-like nitrogen was the main component in the samples of 20% $\text{g-C}_3\text{N}_4$ -TiO<sub>2</sub>-400, while the graphitic nitrogen was the main N species in the sample obtained at 600 °C.

Furthermore, from the C1s spectra (Fig. 4C), it could be observed that the peak of 287.3 eV (C=N) in the sample of 30% $\text{g-C}_3\text{N}_4$ -TiO<sub>2</sub>-600 disappeared and the peak of 288.1 eV (C–N, namely three coordination C, denoted as C<sub>3c</sub>) shifted to 288.9 eV (two coordination C<sub>2c</sub> transformed from C<sub>3c</sub>) comparison with that of 20% $\text{g-C}_3\text{N}_4$ -TiO<sub>2</sub>-400 sample. The reason was that pyridine-like (N-sp<sup>2</sup>C) nitrogen was two coordination and easily be oxidized to break [30,38] and result in the formation of C<sub>2c</sub> in the thermal treatment. According to the literature [36], the graphitic nitrogen was favorable to form the  $\pi$ -conjugated system and that was beneficial to the carriers transport. Namely, 30% $\text{g-C}_3\text{N}_4$ -TiO<sub>2</sub>-600 exhibits a larger positive valence band potential than 20% $\text{g-C}_3\text{N}_4$ -TiO<sub>2</sub>-400 (see Fig. 4D), which is why it exhibits better oxidation ability and photocatalytic activity than the latter.

### 3.3. The photophysical behaviors of photoexcited carriers of the samples

The photophysical behaviors of photogenerated charge carriers in the samples were analyzed by combining UV-vis diffuse reflectance spectrometry (denoted UV-vis DRS) with fluorescence emission spectra. UV-vis DRS was generally used for illustrating the strength of light absorption ability. As shown from Fig. 5A, all the samples possessed the excellent visible light absorption



**Fig. 6.** (A) The samples of PL intensity@425 nm in  $2 \times 10^{-3}$  M NaOH solution with presence of  $5 \times 10^{-4}$  M terephthalic acid, (B) Photocurrent-time curves of the investigated photocatalysts at certain interval time under visible light ( $\lambda \geq 420$  nm) irradiation and the photocatalytic mechanism diagram of (C) traditional heterojunction and (D) Z-scheme construction in the sample of g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>.

ability at 390–600 nm except for the sample of 30%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-600. Fig. 5B was the curves of the converted by Kubelka-Munk (KM) functions as the function of light energy of the investigated samples. According to Fig. 5B, the estimated bandgaps were 2.63, 2.66, 2.83 and 3.03 eV corresponding to the samples of bulk g-C<sub>3</sub>N<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub> nanosheets, 20%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-400 and 30%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-600, respectively. The bandgap of g-C<sub>3</sub>N<sub>4</sub> nanosheets was increased by 0.03 eV than that of bulk g-C<sub>3</sub>N<sub>4</sub> which should be due to the quantum confinement effect. Moreover, the bandgap of 20%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-400 and 30%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-600 is decreased by 0.37 eV and 0.17 eV as compared with that of anatase TiO<sub>2</sub> (3.2 eV), which implies that 20%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-400 and 30%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-600 could exhibit higher light absorption efficiency than the commercial anatase TiO<sub>2</sub>.

Usually, the larger specific surface areas and the stronger UV-vis light absorption ability could result in the better photocatalytic effect because of the more reaction active sites and photogenerated carriers. However, an increased light absorption ability of photocatalysts does not always mean an increased photocatalytic activity, unless the photocatalysts possess a low enough photoexcited electron-hole recombination rate. That was the reason why 20%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-400 sample had the larger specific surface areas (seen in Fig. S4 and Table S1) and the better visible light absorption (seen in Fig. 5A) but had the worse photocatalytic activity than that

of 30%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-600 sample. So the high charge separation and transfer efficiency were the key factors for improving the activity.

According to the fluorescence peak intensity in the fluorescence emission spectra of a catalyst, the charge separation and transfer efficiency could be estimated. Fig. 5C showed that the fluorescence intensity of g-C<sub>3</sub>N<sub>4</sub> nanosheets, 20%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-400 and 30%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-600 decreased obviously compared with that of the bulk g-C<sub>3</sub>N<sub>4</sub> which further indicated that the recombination rate of photogenerated electrons and holes decreased. The fluorescence emission peak of bulk g-C<sub>3</sub>N<sub>4</sub> located at about 470 nm corresponding to the bandgap of 2.63 eV and the fluorescence emission peak position of g-C<sub>3</sub>N<sub>4</sub> nanosheets, 20%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-400 and 30%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-600 took place obvious blue shift which was consistent with the results of UV-vis diffuse reflectance spectra. This further indicated that the thickness of g-C<sub>3</sub>N<sub>4</sub> nanosheets in the composites was decreased (seen in Fig. 2E and F), and which did favor for the transfer of the charge carriers, and leading to a higher photoactivity.

From the ESR results of Fig. 5D, 20%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-400 sample only contained the signal of single-electron trapped oxygen vacancy (denoted as V<sub>o</sub><sup>•</sup>, g=2.001), while 30%g-C<sub>3</sub>N<sub>4</sub>-TiO<sub>2</sub>-600 sample possessed the signals of V<sub>o</sub><sup>•</sup> and g=1.978 which was assigned to the paramagnetic Ti<sup>3+</sup> center [39]. The reason was that g-C<sub>3</sub>N<sub>4</sub> would partially decompose and release reducing gas NH<sub>3</sub>

**Table 1**

The best fitted parameters of time-resolved fluorescence decay spectra.

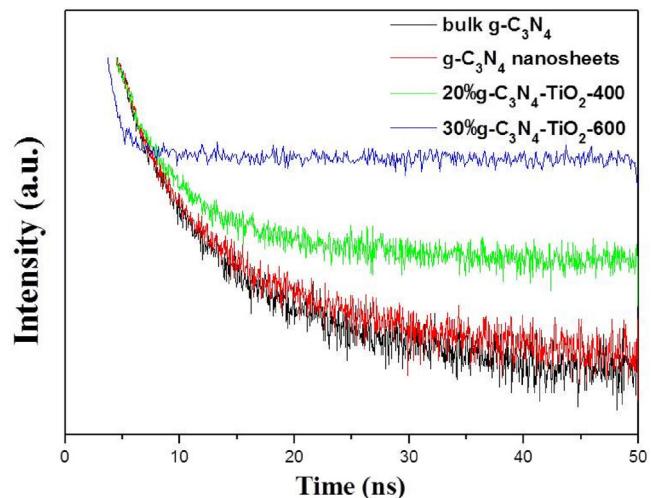
Sample	$\tau_1$ (ns)-Rel%	$\tau_2$ (ns)-Rel%	$\tau_3$ (ns)-Rel%	Goodness of fit parameter ( $\chi^2$ )
Bulk $\text{g-C}_3\text{N}_4$	2.048–39.98	9.009–60.02	–	1.070
$\text{g-C}_3\text{N}_4$ nanosheets	2.162–43.02	10.05–56.98	–	1.132
20% $\text{g-C}_3\text{N}_4$ - $\text{TiO}_2$ -400	1.535–19.62	4.103–44.49	17.23–35.9	1.073
30% $\text{g-C}_3\text{N}_4$ - $\text{TiO}_2$ -600	0.8084–54.61	11.96–45.39	–	1.190

at 600 °C in air which could reduce a part of  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$ , as the evidence by relevant XPS Ti 2p spectra of 20% $\text{g-C}_3\text{N}_4$ - $\text{TiO}_2$ -400 and 30% $\text{g-C}_3\text{N}_4$ - $\text{TiO}_2$ -600. The emerging  $\text{Ti}^{3+}$  would become the segregated center of photoinduced carrier and enhance the separation efficiency [25], thus could improve the photocatalytic activity of the sample. In addition, as shown from Fig. 5D, the bulk  $\text{V}_0^\bullet$  concentration of 600 °C sample was far lower than that of 400 °C sample. In our previous work [35,40],  $\text{V}_0^\bullet$  usually was the recombination center of photo-generated  $\text{e}^-$ - $\text{h}^+$ , so the higher bulk  $\text{V}_0^\bullet$  concentration was harmful to the photocatalytic reaction.

### 3.4. Photocatalytic mechanism of $\text{g-C}_3\text{N}_4$ - $\text{TiO}_2$ heterojunction for propylene oxidation

In order to distinguish the photocatalytic mechanism was the Z-scheme structure (seen in Fig. 6D) or the traditional heterojunction construction (seen in Fig. 6C), the  $\text{g-C}_3\text{N}_4$ - $\text{TiO}_2$  composites was carried out the test of capturing hydroxyl radical using terephthalic acid as probe molecule by fluorescence method. On account of terephthalic acid could only react with dissociative hydroxyl radical to form 2-hydroxyterephthalic acid and emit fluorescence at about 425 nm, the intensity of fluorescence peak at 425 nm could indicate the concentration of dissociative hydroxyl radical. Fig. 6A showed that both the two samples of 30% $\text{g-C}_3\text{N}_4$ - $\text{TiO}_2$ -600 and 20% $\text{g-C}_3\text{N}_4$ - $\text{TiO}_2$ -400 could generate large amounts of dissociative hydroxyl radical under visible light irradiation and 30% $\text{g-C}_3\text{N}_4$ - $\text{TiO}_2$ -600 possessed stronger ability of generating hydroxyl radical arising from its stronger oxidizability at valence band than that of 20% $\text{g-C}_3\text{N}_4$ - $\text{TiO}_2$ -400 (seen in Fig. 4D). While bulk  $\text{g-C}_3\text{N}_4$  and  $\text{g-C}_3\text{N}_4$  nanosheets could produce hydroxyl radical attributed to the reaction of  $\text{OH}^\bullet$  in the water with superoxide radical deriving from surface adsorption oxygen obtained conduction band electrons of  $\text{g-C}_3\text{N}_4$ . That indicated that the photo-oxidation mechanism of propylene by the  $\text{g-C}_3\text{N}_4$ - $\text{TiO}_2$  heterojunction was the Z-scheme system, not the traditional heterojunction structure. The Z-scheme system can keep the stronger oxidation and reduction ability of the valence and conduction charge carriers, thereby resulting in increased photocatalytic activities.

To further inspect the separation ability of the photo-induced electrons and holes, we performed the photocurrent tests at an interval time with periodic visible light irradiation (as shown in Fig. 6B) and time-resolved fluorescence decay spectra measurement (seen in Fig. 7 and Table 1). Fig. 6B showed that the results of all the samples were consistent with their photoactivity; and in particular, 30% $\text{g-C}_3\text{N}_4$ - $\text{TiO}_2$ -600 exhibits the highest photocurrent density (corresponding to the best photoinduced charge separation ability). Fig. 7 indicated that all the curves presented exponential attenuation and  $\text{g-C}_3\text{N}_4$ - $\text{TiO}_2$  composites decayed more slowly than that of the pure  $\text{g-C}_3\text{N}_4$  which demonstrated the photoexcited charge carriers in the  $\text{g-C}_3\text{N}_4$ - $\text{TiO}_2$  composites had the longer lifetime. More important, the high separation efficiency of photoexcited carriers rather than the high lifetime of the charge carriers plays a key role in terms of the photocatalytic activity of the as-prepared photocatalysts. Therefore, 30% $\text{g-C}_3\text{N}_4$ - $\text{TiO}_2$ -600 photocatalyst containing thin and porous plane structure could have promising potential in accelerating the photocatalytic degradation

**Fig. 7.** The time-resolved fluorescence decay spectra of as-prepared photocatalysts.

of organic pollutant like propylene, due to its ability to improve charge separation efficiency and facilitate fast carrier transport.

## 4. Conclusions

A series of  $\text{g-C}_3\text{N}_4$ - $\text{TiO}_2$  direct contact Z-scheme heterojunction composites were prepared via simple annealing the mixture of NTA and bulk  $\text{g-C}_3\text{N}_4$  at different temperatures and it was found that the temperature had significant impact to the photocatalytic activity of the composites. That was mainly due to the influence of calcination temperature to the structure of  $\text{g-C}_3\text{N}_4$ . Particularly, in association with the considerable decrease of the bulk  $\text{V}_0^\bullet$  concentration, the annealing at an appropriate temperature (e.g., 600 °C) affords  $\text{Ti}^{3+}$  with a good ability to separate photo-generated carrier. Therefore,  $\text{g-C}_3\text{N}_4$ - $\text{TiO}_2$ -600 composite photocatalyst, without pyridine-like nitrogen and containing graphitic nitrogen as the major N species as well as thin-porous  $\text{g-C}_3\text{N}_4$  nanosheet structure and  $\text{Ti}^{3+}$ , exhibits the best photocatalytic activity towards the visible light photocatalytic degradation of organic pollutant like propylene. Meanwhile, the hydrogen generation activity of  $\text{g-C}_3\text{N}_4$ - $\text{TiO}_2$ -600 composites was about 2 times than that of  $\text{g-C}_3\text{N}_4$ - $\text{TiO}_2$ -400 composites under UV-vis and visible light irradiation. This can be attributed to the polyporous construction of  $\text{g-C}_3\text{N}_4$  nanosheets in the composites of 600 °C arising from the decomposition of  $\text{g-C}_3\text{N}_4$ , the more positive valence band potential resulted in stronger oxidizing ability. In summary, the direct Z-scheme heterojunction effect, in association with the desired charge transfer and separation efficiency between  $\text{g-C}_3\text{N}_4$  nanosheets and novel  $\text{TiO}_2$ , makes it feasible for  $\text{g-C}_3\text{N}_4$ - $\text{TiO}_2$ -600 to be used as a promising photocatalyst for the degradation of organic pollutant like propylene under visible light irradiation.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.04.061>.

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